Diffusion of H through Pd Membranes: Effects of Non-ideality on D_H and E_D

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Abstract

H diffusion constants, D_H, have been obtained from steady-state fluxes across Pd membranes with the downstream side maintained at $p_{H2}\approx 0$. Good linearity of plots of H flux versus (1/d), where d is the thickness, attests to the H permeation being bulk diffusion controlled in this temperature (423 to 523K) and p_{H2} range ($\leq$ 0.2 MPa). D_H values have been determined at constant p_{up} and also at constant (H/Pd)=*r* conditions.

H fluxes through Pd membranes with three different surface treatments have been investigated (polished (un-oxidized), oxidized, and palladized) in order to determine the effects of these pre-treatments. The palladized and oxidized membranes give similar D_H values but the polished membranes give values about 12% lower.

For diffusion in a concentration gradient $D_H^*(c_H/RT)(d\mu_H/dx)$ is the more proper description, where c_H is the H concentration, rather than $D_H(dc_H/dx)$ where D_H and D_H^* are the concentration-dependent and independent diffusion constants. D_H^* can be obtained from D_H using the thermodynamic factor, $D_H(r) = D_H^*(\partial \ln p_{H2}^{1/2}/ \partial \ln r)_T = D_H^* f(r)$. In the commonly employed situation where there is a large difference in concentrations between the upstream and downstream sides of a membrane, the thermodynamic factor varies with distance through the membrane and this should be allowed for in obtaining D_H^*. Procedures are given and utilized for using $D_H(c_H)$ to determine D_H^* values when there is a large concentration gradient through the membrane.

Activation energies for diffusion, $E_D(c_H)$, have been determined. E_D is found to increase with c_H which can be attributed to the thermodynamic factor. D_H^o values have been found to increase with H content.

Introduction

It is relatively easy to obtain clean Pd surfaces since any oxides are reduced upon exposure to H_2 at moderately high temperatures. Pd alloys are employed for H purification by selective permeation through the alloy membranes. There have been many investigations of H diffusion through Pd, e.g., [1-7]. Studies in the literature cover a wide temperature range which Völkl and Alefeld [7] have summarized by an Arrhenius plot of these D_H data up to 1978 from about 273 K to about 873

K. Although a single straight line is drawn through the data, it seems that the slope, - E_D/R, should vary with temperature as discussed below.

Despite the large number of investigations, some aspects of H diffusion behavior in Pd have not been examined in detail such as the dependences of D_H , D_H^o, and E_D on H concentration in the dilute α phase and this will be done here over a temperature range of interest for H purification through Pd membranes (423 to 523 K). Pd and its alloys are the most suitable systems to investigate the effects of non-ideality of dissolved H because their membranes generally exhibit quite reproducible behavior, there are large H_2 solubilities, and isotherms can be readily determined to evaluate the non-ideality.

Two types of non-ideality must be considered in H permeation through membranes. The first arises from deviations from Sieverts' law of ideal solubility, i.e., when $r \neq K_s\, p_{H2}^{1/2}$, and the other is due to the concentration dependence of Fick's diffusion constant [8], $D_H(r)$, which will be of concern here.

The equation relating the concentration-dependent, $D_H(r)$, and concentration-independent, D_H^*, diffusion constants is given by [8]

$$D_H(r) = D_H^* \left(\partial \ln p_{H2}^{1/2} / \partial \ln r \right)_T = D_H^* f(r) \qquad (1)$$

where $f(r) = \left(\partial \ln p_{H2}^{1/2} / \partial \ln r \right)_T$ and is referred to as the thermodynamic factor, and r = (H/Pd) atom ratio which is convenient to employ where it is appropriate rather than c_H.

In the 1960's Wicke and his students carried out ground breaking research in this area using Pd-H and Pd alloy-H systems [8]. D_H^* values were derived by them from $D_H(r)$ values for Pd and for some Pd-Ag alloys using equation (1) which was appropriate for conditions where the H concentration in the membrane could be assumed to be nearly constant. Their measurements on Pd-H were made in the very dilute range where $f(r)=1$ or else in the concentrated hydride phase where $f(r)>1.0$. The latter caused $D_H(r)$ to increase by a factor of ~10 compared to the dilute region! Since these workers generally investigated diffusion near room temperature, where the dilute phase in Pd-H is limited to small values, the concentration dependence was only investigated at the two extremes of very dilute or very concentrated.

Züchner and coworkers [9,10] and also Küssner [11], who were Wicke's students, employed time-lag techniques where a pulse of H is deposited, generally electrochemically, at the upstream side of a Pd or Pd-alloy membrane. The time for the perturbation to reach the downstream side can be used to calculate D_H. Since the H concentration is initially uniform and the perturbations do not change the uniformity significantly, equation (1) can be employed using an average membrane concentration in $f(r)$.

Both Küssner [11] and Züchner and coworkers [9,10] determined the concentration dependence of D_H for $Pd_{0.77}Ag_{0.23}$ and $Pd_{0.6}Ag_{0.4}$ alloy membranes which were chosen because they have no plateau regions at T≥298K allowing D_H to be measured as a continuous function of r. For the former, D_H decreases from about 3 to 0.4 x 10^{-7} cm^2/s from r=0 to 0.18 at 303K and for the latter, D_H is constant at 3 x 10^{-7} cm^2/s to about r=0.09 and then increases to 13.0 x 10^{-7} cm^2/s at r=0.23. There have been

no measurements of D_H as a continuous function of H content for Pd-H because of hydride phase formation and the limited dilute solubility of H_2 in Pd at moderate temperatures. In this work D_H will be measured at a higher temperature range where greater H contents can be achieved before hydride phase formation takes place.

A complication in the present permeation experiments is that the H concentration is not uniform but varies from r_{up} to 0 at r_{down} and therefore equation (1) cannot be employed directly, where up and down refer to the high and low pressure sides of the membrane. Recently a procedure has been given for determining Fick's diffusion constants from the concentration-dependent ones for this steady state situation [12].

Experimental

In the present experiments fluxes are determined from the decrease of p_{H2} on the upstream side of the Pd membrane while the downstream side is kept at $p_{H2}\approx 0$. Changes were followed using a sensitive electronic diaphragm gauge. Steady state fluxes are established very rapidly for these Pd membranes at the temperatures employed (423-523 K). The decrease of p_{up} during measurements is small because the upstream volume is large and, in any case, the fluxes can be corrected for the small p_{up} decreases resulting from the permeation. Generally however, the fluxes were taken as the initial ones before any appreciable decrease of p_{up}.

The areas of the membranes were all the same, 1.77 cm^2, and a variety of thicknesses were employed. Temperatures were controlled to about ± 1°C and temperature controller settings were verified with a thermocouple in contact with the membranes in the permeation system and these agreed very closely with the temperature controller setting.

Some Pd membranes were cleaned carefully and employed directly and these will be referred to as polished. Some were oxidized in the atmosphere for ~30m at 953K before employing because this procedure has been shown [13] to improve membrane reproducibility. Since oxides formed by Pd do not penetrate into the alloy appreciably and are rapidly reduced in the presence of H_2, their thicknesses will be taken as those before oxidation or palladization. Palladized membranes were prepared by coating them electrolytically with Pd black in a weakly acidic solution of $PdCl_2$.

Results and Discussion

In this research D_H values will be determined from 423 to 523 K in the dilute phase of Pd over the temperature range. An advantage of this is that simple models such as the mean field, lattice gas model, which is conveniently referred to as a regular interstitial solution (RIS) model [19], describe the thermodynamics relatively well in this dilute region. In addition, measurement at low H content avoids problems connected with site blocking which occurs at high H content [8].

The flux and specific permeability of H for the present experiments, where the downstream side is maintained at $p_{H2}\approx 0$, are given by

$$J \quad (\text{mol H/s})/\text{area} \quad = \quad -D_H(dc/dx) \approx -D_H c_{up}/d \qquad (2)$$

$$P \quad (\text{mol H/s})\text{d/area} = -D_H K_s p^{1/2}_{up} \qquad (3)$$

where J is the flux, *P* the specific permeability, d the membrane thickness and K_s a temperature dependent constant relating $p_{H2}^{1/2}$ to *r* via Sieverts' law. In the present experiments the flux, J, and specific permeabilities, P, have been measured. The diffusion constants were then derived from these using H_2 isotherms measured here.

This paper will be organized as follows: (*i*) isotherms (423-523 K), (*ii*) demonstration of the slow step as bulk diffusion rather than surface control, (*iii*) effect of surface treatments of the Pd membranes on D_H, (*iv*) temperature dependence of E_D, (*v*) theory of the effect of non-ideality arising from $f(r)\neq 1.0$ on D_H, (*vi*) procedures for correction of $D_H(r)$ to D_H^*, (*vii*) dependence of E_D on H concentration, *(viii*) effect of non-ideality ($f(r)\neq 1.0$) on D_H^o, (i*x*) concentration profiles during permeation under non-ideal conditions.

i. Dilute Phase Isotherms for Pd-H

Dilute phase H_2 isotherms were measured for Pd at the same temperatures as the diffusion constants (423-523 K) and they are shown as plots of $\ln p_{H2}^{1/2}$ against $\ln r$ in Figure 1 where the ideal slope of 1.0 is shown by the dashed straight line. It can be seen that the slopes are all ≤ 1.0 and the deviation from 1.0 increases with *r* and with decrease of temperature. Thermodynamic factors, i.e., slopes, $(\partial \ln p_{H2}^{1/2}/\partial \ln r)_T = f(r)$ (eqn. 1), have been evaluated from these plots.

ii. Dependence of J upon 1/d at constant p_{H2} and T

These Pd membranes were oxidized as described above. In our earlier studies it was shown there is a linear relation between the permeabilities and $p_{H2}^{1/2}$ as $r \rightarrow 0$ and, if allowance is made for deviations from Sieverts' law of ideal solubility [13], the relationship becomes linear over a large range of *r* at 473 K [13]. A possible role of the thermodynamic factor was not considered in this permeation test for bulk diffusion and this could be a factor at the higher p_{H2}. In view of this, it is desirable to demonstrate that bulk diffusion is the controlling step under conditions where the thermodynamic factor does not play a role and for temperatures other than 473 K.

A better test that bulk diffusion is rate controlling than the linearity of J vs. $p_{H2}^{1/2}$ is a linear relationship between J and (1/d). Such experiments were carried out here with a large number of different membrane thicknesses from 91 to 480 μm. Results are shown in Figure 2 at both 423K and 523 K. Both plots extrapolate to the origin as expected and are linear over the whole range even at the higher fluxes found at 523 K. Moreover, any non-ideality from $f(r)\neq 1.0$ will not affect the linearity since r_{up} and temperature are held constant in these flux measurements. Therefore $f(r)$ will be a constant factor at each d. It can therefore be concluded that bulk diffusion is the rate controlling step in the present experiments.

iii. The Effect of Surface Treatments of Pd Membranes on D_H

Permeation measurements were carried out with Pd membranes (~120 μm thick) which had *not* been oxidized (polished), with membranes had been oxidized, or else which had been palladized.

The polished membrane was carefully cleaned and appeared quite shiny. Measurements were made with these three different surface treatments at a series of *r* values and temperatures. The data were quite reproducible for the oxidized and palladized membranes but less so for the polished one. Results are shown in Table 1 for 423, 473, and 523 K. Similar data were obtained at 453 and 503 K but are not shown. At a given *r*, e.g., 0.020, D_H for the oxidized and palladized surfaces are greater than that for the polished membrane at these temperatures. The differences appeared to increase with increase of temperature, for instance, the decrease from oxidized to polished is 11% at 473 to 523 K and for 453 and 423 K the decreases are 14 and 18%, respectively. The D_H for the palladized and oxidized membranes can be considered to be the same in view of the errors in measurements of d.

Table 1. $D_H(r)$ in units of cm^2/s for the Three Different Surface Treatments of Pd Membranes: oxidized (122 µm), palladized (104 µm), polished (119 µm)

r	$D_H \times 10^6$ (oxididized)	$D_H \times 10^6$ (palladized)	$D_H \times 10^6$ (polished)
423K			
0.010	-	-	-
0.015	6.14	-	-
0.020	6.08	6.11	5.24
0.025	6.03	6.10	5.28
0.030	5.96	5.95	5.15
0.035	5.69	5.72	4.91
0.040	5.49	5.54	4.85
0.045	5.33	-	-
473K			
0.010	13.08	-	-
0.015	12.81	13.41	11.50
0.020	12.79	13.32	11.48
0.025	12.58	13.26	11.27
523K			
0.010	22.89	23.52	20.55
0.015	22.91	23.35	20.49
0.020	22.92	23.16	20.46
0.025	22.92	23.22	20.30

The surface areas of the oxidized and palladized membranes are larger [14] than that of the polished membrane and therefore more H_2 dissociation will take place on these. However the areas appropriate for equations 1 and 2 are the inner ones because the rate-controlling diffusion step within the bulk phase takes place below the outer surfaces and therefore the diffusion areas are the same for all three membranes.

Arrhenius' plots of ln D_H against 1/T for the three different surface treatments are shown in Figure 3 at r =0.02 where it can be seen that the polished membrane has smaller D_H values over the whole temperature range as compared to the other two. From the slopes, the activation energies, E_D, are 24.7, 24.5 and 24.9 kJ/ mol H for the palladized, oxidized and polished membranes, respectively. Similar results were obtained for r=.025. The purpose of the Figure is to illustrate the differences between the three surface treatments at the various temperatures and not to obtain concentration-independent E_D^o values, which will be derived below.

The differences between the various Pd membrane surfaces may partially explain some results in the literature. Examination of these in Table 2 suggests that the D_H values for palladized and oxidized membranes are greater than those for the polished membranes. In the work of Jost and Widmann [4,5] Pd spheres were coated with Pd black and they reported 13.7 x 10^{-6} cm^2/s at 473 K which is certainly relatively fast and close to that in Table 1 for the palladized or oxidized membranes. The value of D_H at 473 K from Bohmholdt and Wicke [6] who employed palladized tubes is somewhat low perhaps due to the extrapolation to 473 K. Another apparent exception to this correlation between the different surface treatments and D_H values appears to be the results of Holleck [1] who employed palladized membranes but D_H values found by him were smaller than those for the palladized or oxidized ones. There is, however, a possibility that some sintering of the Pd black took place because he carried out measurements up to 913 K. Aside from these results, larger D_H values appear to be found for palladized or oxidized Pd membranes.

Table 2. D_H^o, E_D, and D_H for pure Pd (423-523 K)

ref.	D_H^o (10^{-3} cm^2/s)	E_D (kJ/mol H)	D_H (10^{-6} (473 K))	T (K-range)	surface
[4,5]	6.0	23.9	13.7	466-576	palladized
[2]	6.0	23.6	14.6	443-563	polished
[3]	4.3	23.4	11.1	486-652	polished
[6]	3.7	24.0	9.7	293-373	palladized
[15]	4.9	24.0	11.0	300-709	polished
[1]	2.9	22.0	10.9	533-913	palladized
[20]	2.5	21.8	9.8	230-1000	all surfaces
[7]	2.9	22.2	10.3	-	-
[8]	5.3	22.8	16.0	273-373	palladized
[21]	3.1	22.3	10.6	423-723	polished
[13]	5.6	23.2	15.5	423-523	oxidized

iv. Dependence of E_D on Temperature

The p_{up} employed in the gas phase permeation studies of Koffler et al [15] was very small, i.e., 0.4 to 0.6 Pa, and r_{up} was consequently very small and in the ideal range where, with reference to equation (1), f(r)=1.0. Their Arrhenius plot for the permeability of H through Pd (their Fig. 4 [15]) can be seen to be very linear from 300 to 709 K with a reported E_P=15.67 kJ/mol H [15]. The following relation holds between the energies for diffusion and permeability[15], i.e.,

$$E_P = E_D + \Delta H_H^o. \qquad (4)$$

where ΔH_H^o is the enthalpy of $(1/2)H_2(g)$ solution at $r \rightarrow 0$. Since it is known that ΔH_H^o varies with temperature [16, 17, 18], E_D must also vary with temperature in order for E_P to be constant. ΔH_H^o is negative while E_D is positive and, since the former becomes less negative with increase of temperature, E_D must decrease with temperature increase.

Holleck [1] first pointed out that E_D must decrease with temperature and in support of this he cited the values of E_D of 23.4 kJ/mol H at 333 K (av) [6] and 22.0 kJ/mol H at 673 K (av) [1]. There have been no other discussions of the temperature dependence of E_D for Pd-H. Since the work of Holleck, ΔH_H^o values have been measured over a wide temperature range by Lässer and Powell for Pd-H [16, 17] and these are supported by earlier work of Kuji et al [18]; these can be used, together with the constant E_P value from [15], to derive E_D at different temperatures as shown in Table 3. It can be seen that there is predicted to be an appreciable temperature dependence of E_D^* where the asterisk indicates the concentration-independent value since Ep and ΔH_H^o are both for infinite dilution of H.

Figure 4 shows a plot of E_D^* from the literature and one from the present work at 473 K plotted against T together with values predicted from equation (4) where it is assumed that the literature values are for infinite dilution which may not be the case. It can be seen that a temperature dependence is predicted and some experimental values from the literature also suggest a temperature dependence of E_D for Pd-H (Fig. 4) which has not been generally appreciated.

Table 3. Derived values of E_D^* from E_P=15.67 kJ/mol H [15] and ΔH_H^o from [16] where the Asterisk indicates Ideal Behavior, f(*r*)=1.0

T/K	E_P (kJ/ mol H)	ΔH_H^o (kJ/mol H)	E_D^* (kJ/mol H)
273	15.67	-10.05	25.7
373	15.67	-9.37	25.1
473	15.67	-8.46	24.1
573	15.67	-7.47	23.1
673	15.67	-6.45	22.1

v. Concentration-Independent Diffusion Constants, D_H^*, from Concentration-Dependent Ones, $D_H(r)$

The condition $r_{up} >> r_{down}$ is very common in H_2 permeation experiments and, indeed, for H_2 purification. For these boundary conditions it is inappropriate to equate $D_H(r)$ with D_H^* at moderate temperatures because non-ideality due to the thermodynamic factor can be significant (equation 1). For conditions where $r_{up} >> r_{down}$ the H concentration varies across the membrane, and the degree of non-ideality will also vary. Recently equation (5) has been proposed for this situation [12].

$$D_H(r) = D_H^* \int_0^{rup} [(\partial \ln p^{1/2}_{H2})/ (\partial \ln r)]\, dr \;/\; \int_0^{rup} dr$$

$$D_H(r) = D_H^* \int_0^{rup} f(r)dr / r_{up}$$

$$D_H(r) = D_H^* F(r_{up})/r_{up}. \qquad (5)$$

where $\int_0^{rup} dr = r_{up}$ and will be indicated as r_{up} in the following.

In the present work D_H^* will be determined from $D_H(r)$ in four different ways: (*a*) directly from $F(r)$ (eqn. 5) using $f(r)$ from the isotherms at these temperatures [20], (*b*) from equation (5) using the lattice gas, mean field (regular interstitial solution (RIS)) model for Pd-H [19] for evaluation of $F(r)$, (*c*) extrapolation of $D_H(r)$ to r=0, and (*d*) use of an average H concentration, i.e., $r_{up}/2=r_{av}$, in equation (1).

a. Direct Use of Equation (5)

Equation (5) can be employed directly by using areas under plots of the slopes, $(\partial \ln p_{H2}^{1/2}/ \partial \ln r)_T = f(r)$, against r. The slopes are obtained from the experimental isotherms (Fig. 1). The $F(r_{up})$ values can be obtained for any r by integration, $\int_0^{rup} f(r)dr$. D_H^* is then given by $D_H r_{up}/F(r)$. A plot of $f(r)$ against r is illustrated in Figure 5 at 423 K up to r=0.055.

b. Mean Field, Lattice Gas (Regular Interstitial Solution Model (RIS))

This simple model for metal-H systems [19] is given by equation (6) where $\mu^E_H \approx g_1(r)$ which will, for convenience, be referred to as the RIS model

$$RT \ln p_{H2}^{1/2} = \Delta \mu_H^o + RT \ln (r/1-r) + \mu^E_H(r) \qquad (6)$$

where g_1 is a constant at a given temperature and represents the first order term in a polynomial expansion in r of $\mu^E_H(r)$. The partial free energy, g_1, has enthalpic and entropic components, i.e., $g_1 = h_1 - Ts_1$. Experimental isotherms are needed to evaluate g_1 and they have been determined earlier for Pd-H [18] and re-determined here from isotherms measured at the same temperatures as the diffusion studies have been carried out.

From $F(r) = \int_0^{rup} f(r)dr$ and equation (6) we obtain

$$F(r_{up}) = -\ln (1-r_{up}) + g_1(r_{up})^2/2RT. \qquad (7)$$

and this result substituted into equation (5) gives

$$D_H = D_H^* F(r_{up})/r_{up} \approx D_H^* (g_1 (r_{up})/(2RT) - \ln(1-r_{up})/ r_{up}) . \qquad (8)$$

c. D_H^* from Extrapolation of $D_H(r)$ to r=0

Equation (8) predicts a linear relation between $F(r_{up})/r_{up}$ and r_{up} at least up to r=0.04 and therefore D_H can be extrapolated to r_{up}=0 to obtain D_H^*. This method does not require non-ideality values for the calculation of $D_H(r)$.

d. D_H^* using an average $r = r_{up}/2$ in equation (1).

An average value of $r_{av} = r_{up}/2$ can be used in equation (1) which works quite well at small r_{up} as seen from equation (7) at small r where the $-\ln(1-r_{up})/r_{up}$ term can be neglected. At high r values the approximation is not as good. This method will not be as useful for some Pd alloys where the relation between f(r) and r is non-linear at smaller r values, e.g., the $Pd_{0.77}Ag_{0.23}$ alloy.

Evaluation of the Various Methods

There is considerable scatter in the values of D_H^* from the various approaches. Method *b* is not very accurate at relatively high r because a linear approximation of $\mu^E_H(r)$, i.e., $g_1 r$, is no longer adequate. Extrapolation of $D_H(r \rightarrow 0)$ is only good if reliable $D_H(r)$ values can be determined at small r. Method *a* should be good over the whole range of r values provided that accurate f(r) are known. Use of an average $r = r_{up}/2$ in equation (1), which is a reasonable approximation for Pd-H at small r, is certainly the easiest method to employ.

***vi.* Concentration Independent D_H^* from Experimental D_H (r) Values**

Both the concentration-dependent and -independent H diffusion constants are important. The former, $D_H(r)$, can be employed to estimate the actual permeabilities under operating conditions of a membrane where non-ideality is a factor. D_H^*, which is unique at each temperature, is of fundamental interest because of its direct relation to the H mobility.

H fluxes were measured at 423, 453, 473, 503 and 523 K at a series of r values for several oxidized Pd membranes. The $D_H(r)$ values *always* decreased or else remained constant with increase of r_{up} in the range employed r= 0 to 0.08. The decreases are due to the thermodynamic factor and its importance is expected to increase with r_{up} and to decrease with increase of temperature. Some results are shown in Table 4 for 423 K up to r_{up}=0.050. Figure 6 shows a plot of these $D_H(r)$ values against r_{up} where $D_H(r_{up} \rightarrow 0)$ is 6.65×10^{-6} cm^2/s and is seen to be in reasonable agreement with the derived values of D_H^* using the equation 8. The D_H^* values are nearly constant at the lower r values, ±0.2 cm^2/s, and then decrease at higher r.

The results using the average $r = r_{up}/2$ are quite close to those from method *a* (Table 4) but at higher r the former values are slightly greater due to deviations from the linear dependence on r (eqn. 8). This is the first time $D_H(r)$ has been systematically measured as a function of r_{up} in the dilute α phase of Pd-H (423-523 K) and this shows an effect of the thermodynamic factor even at quite low r values, e.g., at r_{up}=0.02, r_{av}=0.01 where there is a significant effect at 423 K.

The trends of these $D_H(r)$ values with r_{up} are quite precise for a given Pd membrane (oxidized) of known thickness and any experimental error is introduced by the flux measurements themselves. When comparing *different* Pd membranes, errors are introduced by the thickness measurements and when comparing with results in the literature errors are also introduced by the area measurements.

Table 4. D_H x 10^6 cm^2/s for Oxidized Pd (76 µm) at 423 K as a function of r and Corrected Values from Procedures *a, b,* and *d*

r_{up}	$D_H(r)$	D_H^* (method *a*)	D_H^* (method *b*)	D_H^* (method *d*)
0.020	5.96	6.45	6.56	6.48
0.025	5.81	6.43	6.56	6.46
0.030	5.68	6.43	6.59	6.45
0.035	5.40	6.27	6.43	6.31
0.040	5.20	6.22	6.37	6.25
0.045	5.06	6.22	6.38	6.27
0.050	4.86	6.15	6.31	6.24

The corrected D_H^* at 503 and 523 K were not as constant as those at the lower temperatures. There appeared to be an overcorrection for the thermodynamic factor at the higher temperatures. $D_H(r)$ was determined for each of these *r*.

The D_H^* derived from D_H using methods *a* or *b* for $T \geq 473$ K increased with *r*, i.e., the thermodynamic factor was too large, which is opposite of the trend at the lower temperatures. The corrections are very sensitive to the magnitude of the thermodynamic factor which has some uncertainty in the present temperature range where there is a steep increase of p_{H2} with *r* for Pd-H. This may be the cause of the under-correction of D_H at low temperatures and over-correction at higher temperatures.

vii. Effect of Non-ideality from the Thermodynamic Factor on E_D

The activation energy for H diffusion in Pd is also affected by the thermodynamic factor which is expected because it must be the main cause of the decrease in D_H with *r*.

An expression for the activation energy for diffusion, $E_D(r)$, determined at a constant r_{up} can be obtained by differentiation of equation (5), i.e.,

$$\partial \ln D_H / \partial (1/T) = \partial \ln D_H^* / \partial(1/T) + \partial \ln F(r_{up})/\partial(1/T) - \partial \ln r_{up} / \partial(1/T) \qquad (9)$$

and

$$E_D = E_D^* - R(\partial \ln F(r_{up}) / \partial (1/T))_{rup} \qquad (10)$$

since at constant r_{up} the ln r_{up} term drops out. In the temperature range of interest (423 to 523 K), E_D^* will be considered to be constant and D_H^o should also be constant in this limited temperature range. There is no accurate way to determine $E_H^{0,*}$ using the average concentration because the derivative in equation (10) cannot be evaluated accurately with the available data at $r_{up}/2$.

An approximate expression for E_D^* can be obtained from equations (7) and (10) based on the RIS model [19].

$$E_D = E_D^* + h_1 r_{up} / [(2\ln(1- r_{up})/ r_{up}) - g_1 r_{up}/RT] \qquad (11)$$

where $g_1 = h_1 - Ts_1$. Since s_1 is negative at small r [18], $h_1 < g_1$, e.g., $g_1 = -32.7$ kJ/mol H and $h_1 = -64$ kJ/ mol H from the present isotherm data at 473 K. Since h_1 is negative for Pd-H and $2\ln(1-r_{up})/(r_{up}) < -g_1(r_{up})/RT$, $E_D(r) > E_D^*$. For example, for $r_{up} = 0.05$, $E_D(r) = 0.05 - E_D^* = 1.9$ kJ/mol H which is an appreciable difference which should be allowed for. Differences between $E_D(r_{up})$ and E_D^* occur even at quite low r, e.g., at $r_{av} \approx r_{up}/2 = 0.01$, E_D is 24.6 compared to $E_D^* = 23.9$ kJ/mol H. This effect of the thermodynamic factor may help to explain variations in E_D values reported (Table 2).

Attempts to determine E_D^* from E_D using equation (10) directly were unsuccessful because values of $(\partial F(r)/\partial (1/T))_{rup}$ determined from the present isotherms (Fig. 1) are not sufficiently accurate. Any evaluation of E_D^* from equation (10) at $r_{av} = r_{up}/2$ would also be unsuccessful. Until more accurate $F(r)$ values are available, E_D^* can be obtained for Pd-H by extrapolation to $r_{up}=0$ or by using equation (11). Another way to determine E_D^* is from an Arrhenius plot of D_H^*. This has been done using $\ln D_H^*$ at $r_{up}=0.025$ which gives a value of 24.1 kJ/mol H and $D_H^{o,*} = 6.1 \times 10^{-3}$ cm^2/s. Other values calculated using different sets of experimental D_H values and different correction procedures to obtain D_H^* ranged from 23.5 to 24.3 kJ/mol H over the present temperature range. The extrapolated value from Figure 7 is about 23.9 kJ/mol H. It seems that it is difficult to give a more precise value than 23.9 ±0.4 kJ/mol H.

Figure 7 shows E_D values as a function of r for a 76 µm Pd membrane and it can be seen that they increase in a non-linear way at higher r values. If these are corrected using equation (11), nearly constant E_D^* values are obtained as shown. The average value of these E_D^* is 23.9 kJ/ mol H which is in good agreement with that predicted from constant E_P (Fig. 4).

Bohmholdt and Wicke [6] determined E_D values at a high and at low H contents (293-373 K) and found that at $r \rightarrow 0$, $E_D = 23.4$ kJ/ mol H and at $r = 0.74$, $E_D = 24.1$ kJ/ mol H, i.e., the change is in the same direction as found here and it should be noted at high H contents the non-ideality cannot be described by the RIS model.

viii. Effect of the Thermodynamic Factor on D_H^o

It can be seen from Table 2 that the D_H^o values change from about 3 to 6 x 10^{-3} which introduces about as much variation into the $D_H(r)$ values as the variations of E_D. If the $\ln D_H^o$ values are extrapolated to $r_{up} \rightarrow 0$, $D_H^{o,*} = 5.25 \times 10^{-3}$ cm^2/s which agrees with the 4.9×10^{-3} cm^2/s given by Koffler et al [15] which should correspond to $D_H^{o,*}$ because of the very low r. The values obtained from the Arrhenius plots of D_H^* to determine E_D^* are from 5.1 to 6.3 x $10^{-3} cm^2/s$ which are in reasonable agreement with those in Table 5.

Besides affecting E_D, the thermodynamic factor affects D_H^o. Bohmholdt and Wicke [6] found that D_H^o is greater in the concentrated phase ($r = 0.70$) than in the very dilute phase which is in the same direction as the trend found here. Equation (12) can be derived from equations (5) and (10)

$$\ln (D_H^{*,o}/D_H^o) = \Delta E_D/RT + \ln [F(r_{up})/(r_{up})] \qquad (12)$$

where $\Delta E_D = E_D^* - E_D$.

If the RIS model is employed to evaluate ln $F(r_{up})/(r_{up})$, we obtain

$$\ln (D_H^{o,*}/D_H^o) = \Delta E_D/RT - \ln [\, g_1 r_{up}/2RT - \ln(1-r_{up})/r_{up} \,] \qquad (13)$$

and the results in Table 5 have been obtained from this equation. When r increases, the increase of E_D dominates over the increase of D_H^o leading to the observed decrease of $D_H(r)$ with r_{up}. It is noteworthy that E_D and D_H^o increase significantly with r_{up} while D_H itself decreases less sharply.

Table 5. D_H^o as a function of r for Pd (423 K)

r	D_H^o x10^{-3} cm^2/s	$D_H^{o,*}$ x10^{-3} cm^2/s
0.010	5.83	5.61
0.015	6.04	5.64
0.020	6.43	5.83
0.025	6.70	5.90
0.030	7.12	5.93

ix. H Concentration Profiles

The role of solute non-ideality on experimental D_H values obtained by fluxes through membranes has been considered by Barrer [23], Crank [24] and Jost [25] where the concentration profile is assumed to be known. They give procedures for the calculation of the thermodynamic factor and D_H^*.

In the present work the concentration profile is unknown but the thermodynamic factor is known and D_H^* can be obtained by the methods above. The concentration profile can then be determined from the following equation, which was derived from equation (6) as given in [12],

$$x/d = [F(r_{up}) - F(r)] / F(r_{up}) \qquad (14)$$

where x is the distance across the membrane and d is the thickness. $F(r)$ can be determined at each r from integration of plots of $f(r)$ against r. Results are shown in Figure 8 for p_{up}=0.050 ($F(r_{up})$=0.0375) at 423 K. It can be seen that at all x except 0 and 1.0, the H concentration is smaller than the ideal value given by the linear relation between r and (x/d).

In the steady state the flux is the same at any x throughout the membrane, i.e., $J = - D_H(c_H)(\partial c_H/\partial x)$ must be constant at all x and corresponding r. These J values must also be equal to the measured steady state value, $D_H(\text{exp})\,(c_{H,up})/d$. The flux is also given by $J = D_H^*\,(c_H/RT)\,(\partial\mu_H\,(c_H)/\partial x)$ which must equal $-D_H(c_H)(\partial c_H/\partial d)$. At each x, the flux must be the same as the experimental flux. The flux at each x is also given by

$$J = D_H^*\, f(r)\, dc_H/dx. \qquad (15)$$

Calculated fluxes are given in Table 6 as a function of x. It can be seen from the Table that the fluxes are generally close to J(exp) and reasonably constant demonstrating the validity of the analysis.

Table 6. Fluxes as a function of x for Pd at 423 K, r_{up}=0.05, d=76 μm and D_H^* = 6.4 x10^{-6} (mol H/s)cm^{-2} where J(exp)=3.6 x 10^{-6} (mol H/s)cm^{-2}

(x/d)	**f(r)** at x	**dc_H/dx** (mol H/ cm^{-3}/cm)	**J** (10^{-6}(mol H/s) cm^{-2})
0	0.56	1.02	3.7
0.07	0.61	0.78	3.7
0.325	0.75	0.75	3.9
0.52	0.85	0.79	3.7
0.75	0.92	0.60	3.5

Conclusions

It has been shown that oxidized and palladized Pd membranes give similar permeation results but the un-oxidized (polished) ones give smaller D_H values. For the first time the dependence of D_H upon r in the dilute phase of Pd-H has been determined and explained in terms of the thermodynamic factor which can be a significant factor even at low H concentrations. There are several ways to determine D_H^* from $D_H(r)$ when there is a large concentration profile through the membrane, i.e., $c_{up}>>c_{down}$. This is a very common situation and pertinent to practical H_2 purification. The results do not differ appreciably in the range examined here between D_H^* values determined from equation (5) and those employing equation (1) with an average H content in the membrane $r_{av}=r_{up}/2$. At higher H contents and for Pd-rich alloys such as $Pd_{0.77}Ag_{0.23}$ this is no longer the case.

E_D increases with r and this can be accounted for by the thermodynamic factor using the RIS model. An illustration of the calculation of a concentration profile is given where the H concentrations are smaller than the ideal ones where there is a uniform gradient over the membrane.

Acknowledgements

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Figure Captions

Fig. 1. H_2 solubilities for Pd. The dashed straight line shows ideal behavior where the slope, i.e., thermodynamic factor, =1.0.

Fig. 2 H_2 flux plotted against 1/d for Pd membranes at 423 and 523 K with p_{up}=50.65 kPa.

Fig. 3 ln D_H plotted against 1/T for several different surface treatments of Pd at r=0.02. ○, unoxidized; Δ, oxidized; ●, palladized

Fig. 4 E_D as a function of temperature. ○, calculated from $E_D = E_P - \Delta H_H^o$; □, from the literature (see Table 2); Δ, present data.

Fig. 5 Plot of the thermodynamic factor against r for Pd at 423 K.

Fig. 6. Plots of D_H against H/Pd at 423 K for Pd (76 μm). ○, experimental data; □, corrected by method (a); Δ, corrected by method (b), ◊, corrected by method (d).

Fig. 7. Plot of E_D against H/Pd for Pd (76 μm) slopes. ○, experimental data; Δ, experimental data corrected using equation (11).

Fig. 8. Plot of H/Pd at various degrees of penetration across a Pd membrane at 423 K and r_{up}=0.050. ○, data calculated from equation (14); solid straight line, ideal behavior where f(r)=1.0.

Figure 1.

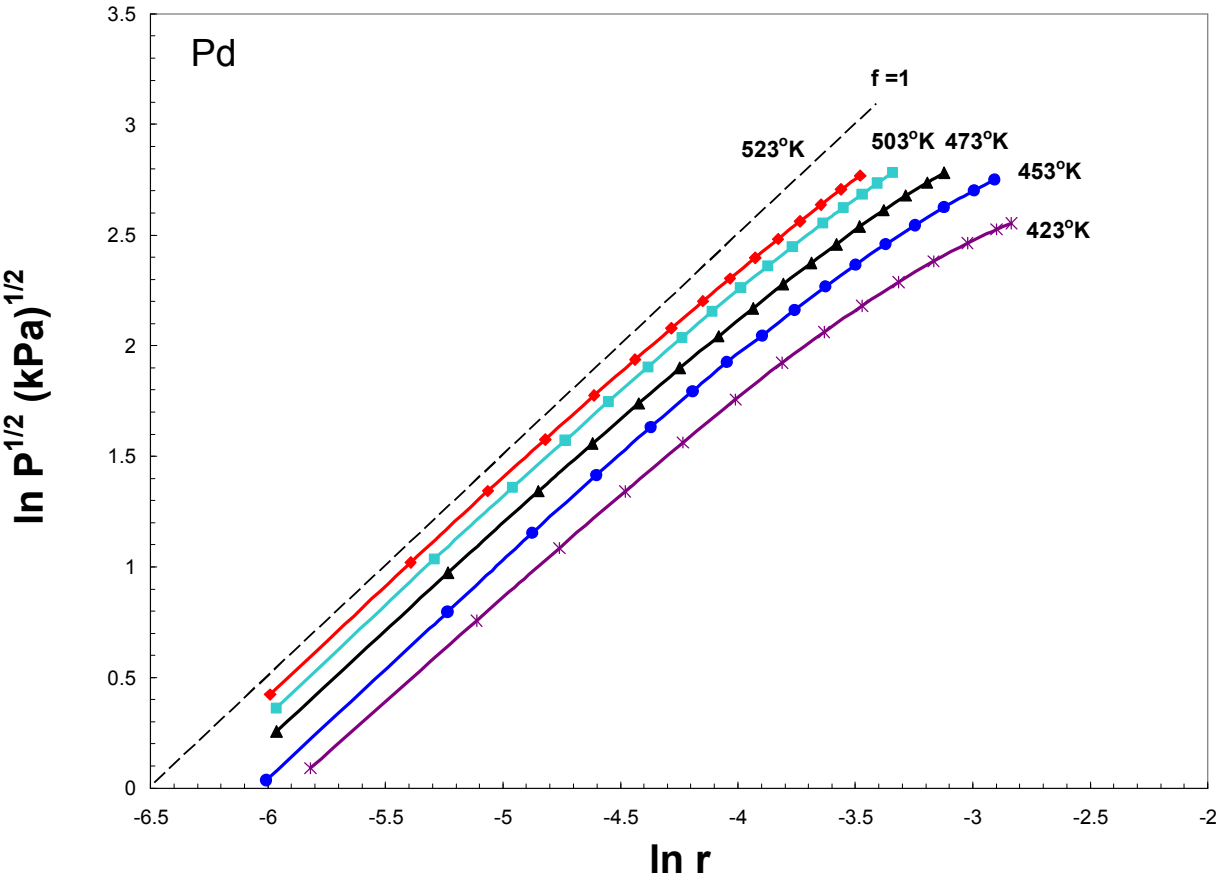
Pd
f =1
523°K
503°K
473°K
453°K
423°K
ln P^1/2 (kPa)^1/2
ln r
3.5
3
2.5
2
1.5
1
0.5
0
-6.5
-6
-5.5
-5
-4.5
-4
-3.5
-3
-2.5
-2

Figure 2.

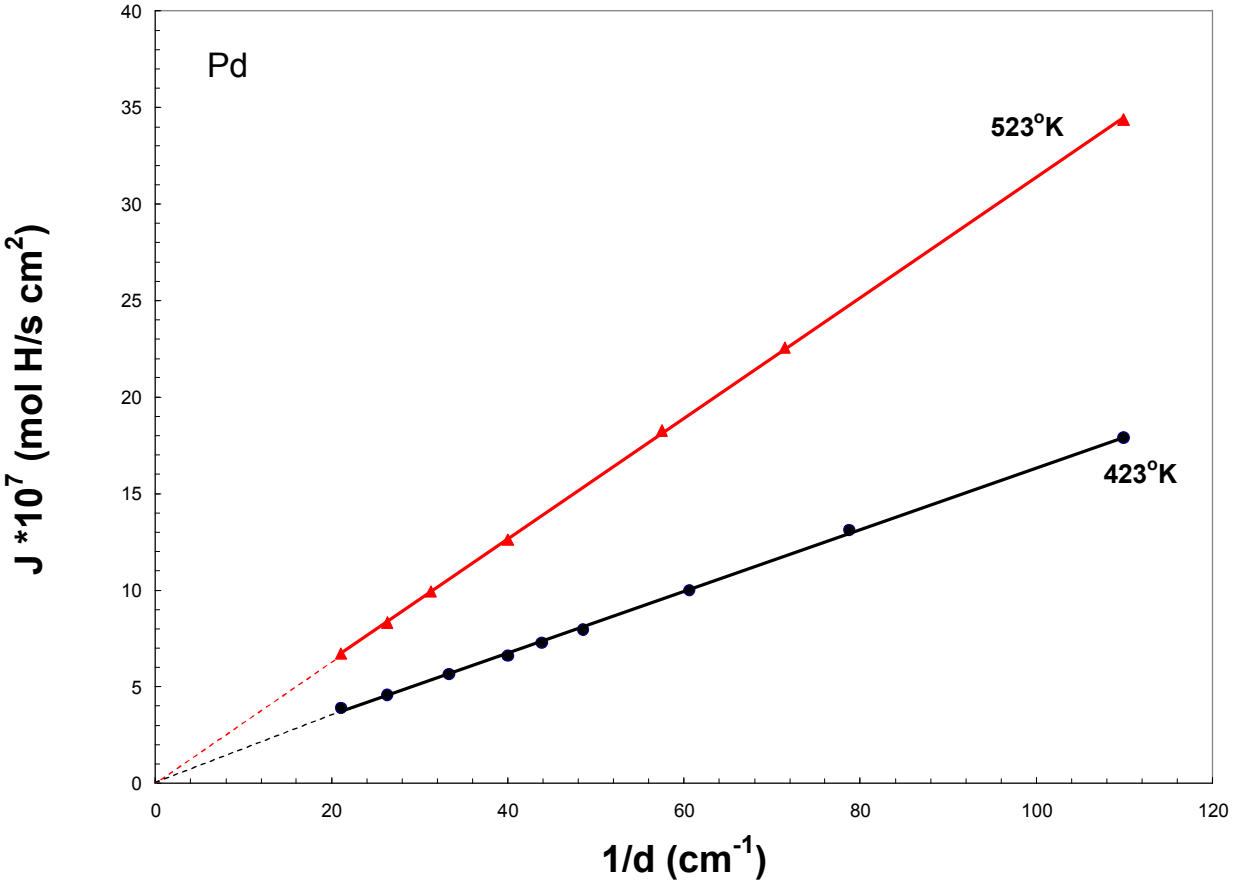
Pd
523°K
423°K
J *10^7 (mol H/s cm^2)
1/d (cm^-1)
0
5
10
15
20
25
30
35
40
0
20
40
60
80
100
120

Figure 3.

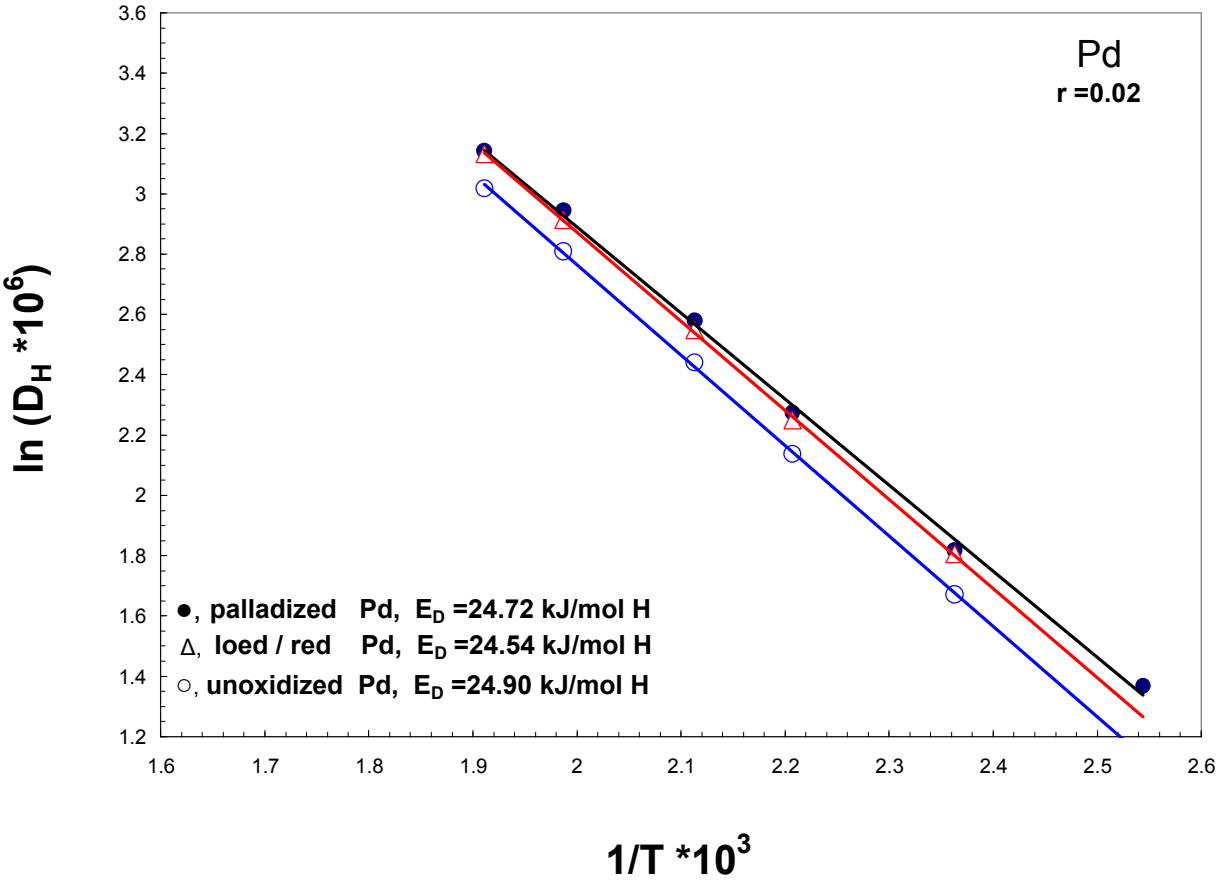
Pd
r =0.02
●, palladized Pd, E_D =24.72 kJ/mol H
Δ, loed / red Pd, E_D =24.54 kJ/mol H
○, unoxidized Pd, E_D =24.90 kJ/mol H
ln (D_H *10^6)
1/T *10^3
3.6
3.4
3.2
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1.6
1.7
1.8
1.9
2
2.1
2.2
2.3
2.4
2.5
2.6

Figure 4.

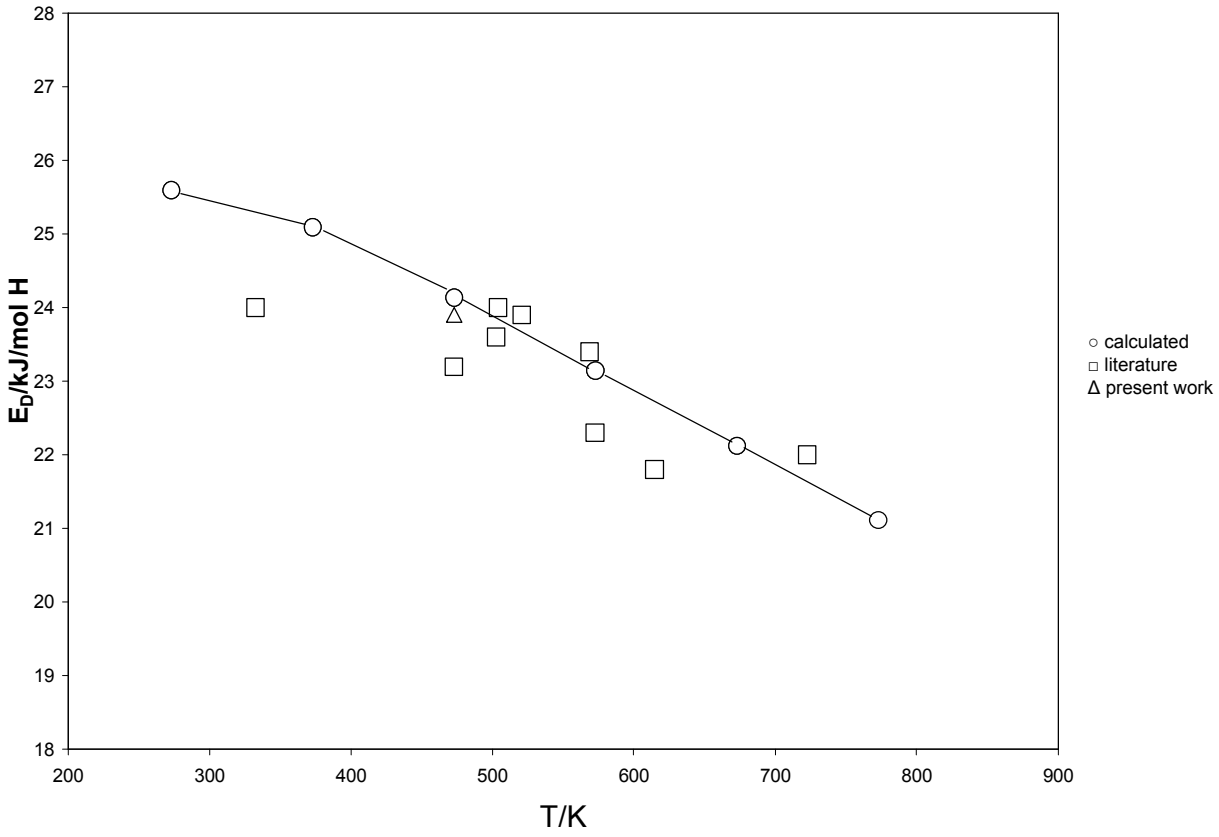
28
27
26
25
24
23
22
21
20
19
18
200
300
400
500
600
700
800
900
T/K
E_D/kJ/mol H
○ calculated
□ literature
Δ present work

Figure 5.

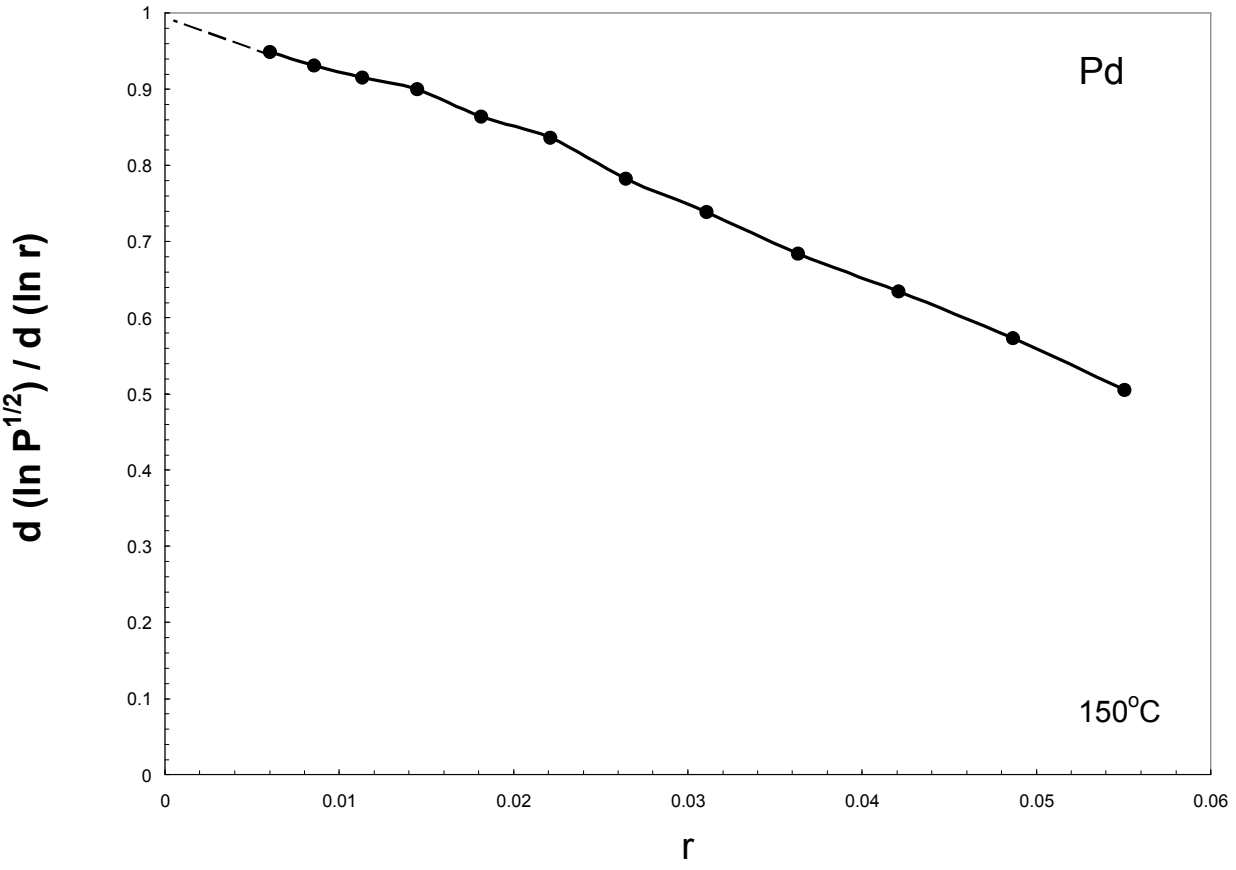
Pd
150°C
d (ln P^1/2) / d (ln r)
r
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
0.01
0.02
0.03
0.04
0.05
0.06

Figure 6.

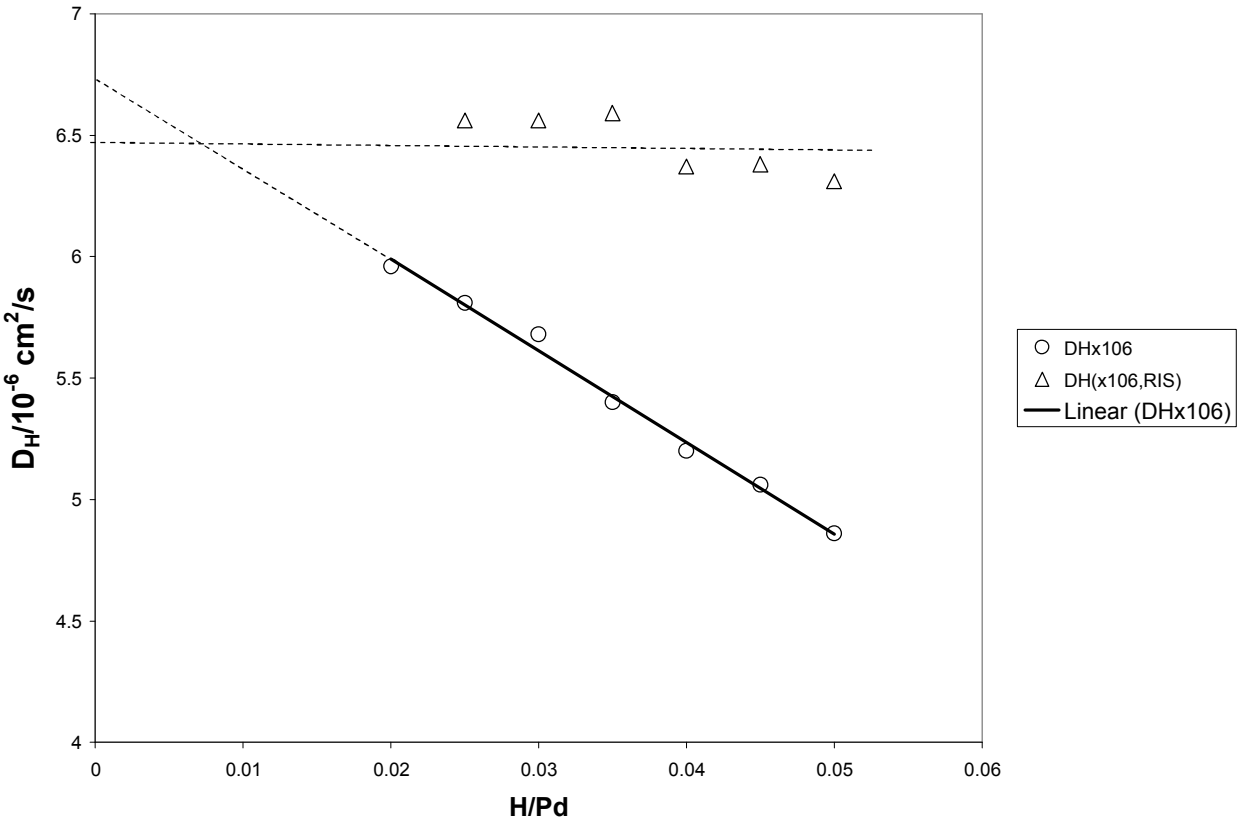
7
6.5
6
5.5
5
4.5
4
0
0.01
0.02
0.03
0.04
0.05
0.06
$D_H/10^{-6}$ cm^2/s
H/Pd
DHx106
DH(x106,RIS)
Linear (DHx106)

Figure 7.

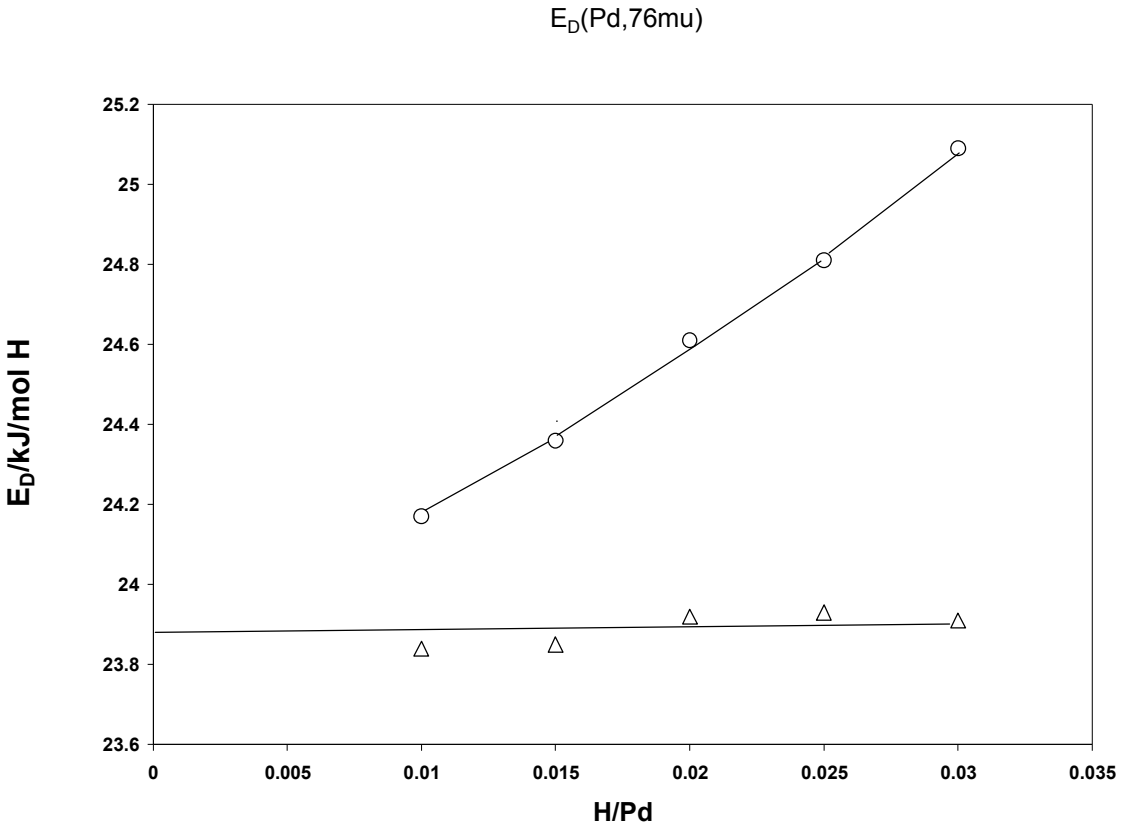
E_D(Pd,76mu)
E_D/kJ/mol H
H/Pd
25.2
25
24.8
24.6
24.4
24.2
24
23.8
23.6
0
0.005
0.01
0.015
0.02
0.025
0.03
0.035

Figure 8.